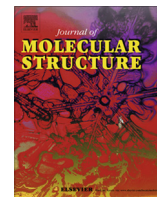




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# Synthesis and spectroscopic characterization of Ru(II) and Sn(IV)-porphyrins supramolecular complexes



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## H I G H L I G H T S

- Ru(II) and Sn(IV)-porphyrins were synthesized.
- 2D DOSY NMR spectra for title compounds were studied.
- The association constants were calculated.

## A R T I C L E I N F O

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## A B S T R A C T

Synthesis and NMR studies of Ru(II) and Sn(IV) tetraphenylporphyrins supramolecular complexes were carried out. The diffusion coefficients of the complexes, porphyrinates, and solvents were determined by DOSY NMR spectroscopy. By the method of spectrophotometric titration a binding ability of Ru(II) tetraphenylporphyrin towards 4-(imidazol-1-yl)-phenol was investigated, stability constant of resulting complexes and concentration intervals of their existence were defined.

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## Introduction

The ability of coordinatively unsaturated Ru(II) and Sn(IV) porphyrins for axial coordination of electron donating molecules or fragments allows them to act as a basis upon designing multifunctional supramolecular ensembles [1–8]. In most cases, donor–acceptor interactions between a cation of the porphyrinate reaction center and nitrogen or oxygen atoms of a substrate are driving forces of these processes. In six-coordinate Ru(II) porphyrins [(Solv)Ru(CO)P] the metal cation can consistently bind two molecules of nitrogen-containing substrate. And, if binding of one (the “first”) molecule of a substrate easily proceeds in the position of a solvent molecule, more narrow terms are necessary for adding another (the “second”) molecule of a substrate in the CO group position [9].

Sn(IV) porphyrins are no less interesting from the point of view of supramolecular porphyrin ensembles creation. They preferably connect oxygen-containing ligands (carboxylates and phenolates) and are complexes with a *trans*-diaxial coordination of ionic or neutral substrates [10–14]. Rather labile carboxylate complexes of Sn(IV) porphyrins are easily formed upon interaction of a carbonic acid with Sn(IV) dihydroxyporphyrin [(OH)<sub>2</sub>SnP] in organic solvents at the room temperature. Rate of the process is defined by acid properties of the organic acid. Steadier phenolate complexes of Sn(IV) porphyrins are formed upon refluxing of phenol with (OH)<sub>2</sub>SnP in benzene or pyridine within several hours [11].

In continuation of our studies in the field of supramolecular chemistry of porphyrins [15–18], in this work synthesis and NMR studies of Ru(II) tetraphenylporphyrin [(H<sub>2</sub>O)Ru(CO)P], (**1**) and complexes of **1** and Sn(IV)porphyrin [(OH)<sub>2</sub>SnP, (**2**)] with 4-(imidazol-1-yl)-phenol [(L, (**3**)] with one [(ImPhOH)Ru(CO)P (**4**), (ImPhO)<sub>2</sub>SnP (**5**)] and two [(ImPhO)Ru(CO)P]<sub>2</sub>SnP (**6**)] centers of binding were carried out. By the method of spectrophotometric titration a binding

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